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<b>(54) Title:</b> FLUORO-CHEMICAL COMPOSITION COMPRISING A POLYURETHANE HAVING A FLUORO-CHEMICAL OLIGOMER AND A HYDROPHILIC SEGMENT TO IMPART STAIN RELEASE PROPERTIES TO A SUBSTRATE			
<b>(57) Abstract</b>  A method for preparing a fluorochemical composition comprising a polyurethane by reacting: (A) fluorochemical oligomer of formula (I): $M^f_m M_n - Q^1 - T^1$ , wherein: $M^f_m M_n$ represents fluorochemical oligomer comprising m units derived from fluorinated monomer and n units derived from fluorine-free monomer and wherein the fluorinated monomers and fluorine-free monomers may be the same or different; m represents a value of 2 to 40; n represents a value of 0 to 20; $T^1$ is -OH or -NH <sub>2</sub> ; $Q^1$ and $T^1$ together represent the organic residue obtained by removing a hydrogen atom from a chain transfer agent that is functionalized with $T^1$ ; (B) difunctional compound capable of reacting with an isocyanate; (C) monofunctional compound capable of reacting with an isocyanate and comprising a poly(oxyalkylene) group with (D) triisocyanate. Substrates treated with fluorochemical compositions prepared according to the method, have good stain release properties, particularly for oily stains and water based stains such as wine, tea and coffee.			

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**FLUOROCHEMICAL COMPOSITION COMPRISING A  
POLYURETHANE HAVING A FLUOROCHEMICAL OLIGOMER AND A  
HYDROPHILIC SEGMENT TO IMPART STAIN RELEASE PROPERTIES  
TO A SUBSTRATE**

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**Field of the Invention**

The present invention relates to fluorochemical compositions for the treatment of substrates, in particular fibrous substrates such as textiles to impart stain release properties to those substrates.

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**Background of the Invention**

Fluorochemical compositions for the treatment of substrates such as leather, textiles, and paper, are well known and are used to impart various properties to the substrate such as water and/or oil repellency, waterproofness, stain release, and anti-staining. For example, U.S. Patent No. 5,276,175 discloses isocyanate derivatives comprising fluorochemical oligomers. In particular, the disclosed fluorochemical compositions comprise fluorinated compounds, wherein the fluorinated compound comprises a fluorochemical oligomeric portion, an organic moiety, and a group that can impart soft hand, stain release, water repellency, or a durable property when applied to a fibrous substrate, and wherein the fluorochemical oligomeric portion is bonded to the organic moiety through an isocyanate-derived linking group. Substrates treated with such compositions are shown to exhibit durable and abrasion-resistant oil and water repellency. Further, in one of the examples, a fluorochemical composition based on a condensate of a tri-isocyanate, a fluorochemical oligomer and a methoxypolyethyleneoxide glycol is described. Stain release properties for this composition were demonstrated on a polyester/cotton blend fabric.

U.S. Patent No. 5,350,795 discloses fluorochemical compositions for treating textile fibers and fabrics to impart oil and water repellency without thermal treatment. The compositions comprise an aqueous, substantially organic-solvent-free, solution or dispersion of (a) a fluorochemical acrylate copolymer comprised of

a fluorinated acrylate monomer, polyalkylene glycol acrylate or methacrylate, or polyalkylene glycol diacrylate or dimethacrylate; and (b) a polyalkoxylated polyurethane having pendant perfluoroalkyl groups comprised of an aliphatic or aromatic tri- or higher order isocyanate, a fluorinated alcohol, amine, or mercaptan, and a poly(oxyalkylene) diol or dithiol.

U.S. Patent No. 4,788,287 and U.S. Patent No. 4,792,354 disclose a water and oil repellent compound having at least two terminal segments and an intermediate segment connecting the terminal segments that has a molecular weight of from 800 to 20,000. Each terminal segment of the compound contains at least one polyfluoroalkyl group connected by a -CONH- linking group, the intermediate segment is a urethane oligomer that contains at least two -CONH- linking groups in one molecule, and the terminal segments and intermediate segment are connected by a -CONH- linking group. The urethane oligomer of U.S. Patent No. 4,792,354 further contains a hydrophilic molecular chain.

U.S. Patent No. 5,491,261 discloses di-, tri- and poly-perfluoroalkyl-substituted alcohols and acids and derivatives thereof which are prepared from perfluoroalkyl iodides and di-, tri- or polyalkyl alcohols or acids. They can be reacted with isocyanates, epoxy compounds, anhydrides, acids or acid derivatives to prepare a great variety of oil- and water-repellent compositions.

Fluorochemical compositions are also used to facilitate stain or soil release from a substrate such as a fabric. Routine treatments of fabrics with various modifying additives such as softeners, stiffeners, and lubricants to impart desired properties to a commercial fabric typically increase the oleophilicity of the fabric, thereby significantly increasing its tendency to accept oily stains and reducing its ability to release such stains after laundering. Fluorochemical compositions based on a mixture of a fluorinated compound and a non-fluorinated hydrophilic compound, or on a chemical "hybrid" compound that contains fluorochemical oleophobic segments ("F") and non-fluorinated hydrophilic segments ("H") are known to act as stain release compositions since they provide oil repellency during normal wear and inhibit wicking or diffusion of oily soils into the fabric or fiber bundles as well as facilitate soil release during laundering.

U.S. Patent No. 3,574,791 discloses a block-copolymer consisting of F and H segments for use as a stain-release agent. The "F"-segments are substantially free of hydrophilic groups whereas the "H" segments are substantially free of fluorinated aliphatic groups. It is taught that due to this segmentation, the polymer is

5 "autoadaptable," i.e., a fabric treated with the polymer will be oil and water repellent in an atmospheric environment, and when laundered in water, it will become hydrophilic so stain removal will become possible. Various possible chemical linkages are contemplated for connecting the "F" and "H" segments, including a urethane linkage derived from the reaction of an alcohol and an

10 isocyanate.

U.S. Patent No. 5,509,939 discloses a fluorochemical composition to impart soil release properties to a substrate. The fluorochemical composition comprises urea-linkage-containing-alkoxypolyoxyalkylene fluorocarbamates prepared by reacting (a) at least one polyisocyanate which contains at least three isocyanate

15 groups with (b) at least one fluorochemical reagent which contains one functional group which has at least one hydrogen atom and at least two carbon atoms each of which contains at least two F atoms, (c) at least one hydrophilic, water-solvatable reagent which contains a single functional group which has at least one reactive hydrogen atom, and (d) at least one reagent which contains one reactive hydrogen

20 atom, and which on reaction with an isocyanate group, yields functionality which has abeyant chemical reactivity with fibrous substrates, and then reacting the product with water, such that reactants (b), (c) and (d) are reacted with 55% to 95% of the isocyanate groups, and water is reacted with the remainder.

Despite the many fluorochemical compositions known to impart stain

25 release properties to a substrate, there continues to be a desire for fluorochemical compositions that have improved properties. Desirable properties for fluorochemical compositions include easy cleanability of natural fiber substrates such as cotton and blends of cotton and polyester, particularly with respect to oil-type stains (dirty motor oil, vegetable oil) and water based stains (tea, coffee); low

30 manufacturing cost; high storage stability; easy emulsifiability and high performance even if applied in low quantities. It is further desirable that the fluorochemical

compositions provide good stain repellency and oil and/or water repellency properties to the substrate.

### Summary of the Invention

5           The present invention relates to a method for preparing a fluorochemical composition comprising a polyurethane by reacting:

(A)   fluorochemical oligomer of formula (I)



wherein:

10        $M_m^f M_n$  represents a fluorochemical oligomer comprising m units derived from fluorinated monomer and n units derived from fluorine-free monomer and wherein the fluorinated monomers and fluorine-free monomers may be the same or different;

m represents a value of about 2 to 40;

15       n represents a value of 0 to about 20;

$T^1$  is -OH or -NH<sub>2</sub> ;

$Q^1$  and  $T^1$  together represent an organic residue obtained by removing a hydrogen atom from a chain transfer agent that is functionalized with  $T^1$ ;

20       (B)   difunctional compound capable of reacting with an isocyanate; and

(C)   monofunctional compound capable of reacting with an isocyanate and comprising a poly(oxyalkylene) group; with

(D)   triisocyanate.

25       The present invention further provides a fluorochemical composition comprising a polyurethane obtainable by the above method and the use of the fluorochemical composition to provide stain release properties to a substrate.

Further provided is the treatment of a substrate using one of the fluorochemical compositions and a substrate treated with one of said fluorochemical compositions.

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**Detailed Description of the Invention**

In connection with the present invention, the term "monofunctional" compound means a compound that contains only one functional group capable of reacting with an isocyanate. The term "difunctional compound" means a compound that has only two functional groups capable of reacting with an isocyanate.

The term "functionalized fluorochemical oligomer" means a fluorochemical oligomer that contains a functional group capable of reacting with an isocyanate.

The fluorochemical composition of the present invention can be prepared in a two step reaction. In a first step, a functionalized fluorochemical oligomer is prepared, which is further reacted to form a polyurethane in the second step.

In the first step, fluorochemical oligomer according to formula (I) is prepared:



wherein:

$M_m^f M_n$  represents fluorochemical oligomer comprising m units derived from fluorinated monomer and n units derived from fluorine-free monomer and wherein the fluorinated monomers and fluorine-free monomers may be the same or different;

m represents a value of about 2 to 40;

n represents a value of 0 to about 20;

$T^1$  is -OH or -NH<sub>2</sub>;

$Q^1$  and  $T^1$  together represent the organic residue obtained by removing a hydrogen atom from a chain transfer agent that is functionalized with  $T^1$ .

The value of m in the fluorochemical oligomer is between about 2 and 40 and preferably between about 2 and 20 and more preferably between about 3 and 15. The value of n can be from 0 to about 20 and is preferably between about 3 and 10. According to a preferred embodiment, the value of n is less than that of m. Fluorochemical oligomers derived from two or more different fluorinated monomers and/or two or more different fluorine-free monomers are within the scope of this invention.

In the above formulas,  $Q^1$  typically represents an organic residue according to the following formula:

-S-R-

wherein:

R represents an organic divalent linking group that is preferably selected from the group consisting of linear or branched alkylenes (preferably having about 2 to 6 carbon atoms), cyclic alkylenes, arylenes and aralkylenes.

The fluorochemical oligomer can be prepared by free-radical oligomerization of fluorochemical monomers ( $R_f-L^1-E$ ) alone or in combination with hydrocarbon monomers ( $R_h-E'$ ), in the presence of hydroxy- or amino-functionalized chain transfer agents. The term "hydrocarbon," in connection with the present invention, means any substantially fluorine-free organic moiety that contains hydrogen and carbon, and optionally, one or more substituents. The aliphatic backbone of the fluorochemical oligomer comprises a sufficient number of polymerized units to render the portion oligomeric. The aliphatic backbone preferably comprises from about 2 to about 40 polymerized units derived from fluorochemical monomers and from 0 to about 20 polymerized units derived from hydrocarbon monomers.

The fluoroaliphatic radical,  $R_f$ , in the fluorochemical monomer, is a fluorinated, stable, inert, preferably saturated, non-polar, monovalent aliphatic radical. It can be straight chain, branched chain, cyclic or combinations thereof. It can contain heteroatoms such as oxygen, divalent or hexavalent sulfur, or nitrogen.  $R_f$  is preferably a fully-fluorinated radical, but hydrogen or chlorine atoms can be present as substituents if not more than one atom of either is present for every two carbon atoms. The  $R_f$  radical has at least about 3 and up to about 18 carbon atoms, preferably about 3 to 14, especially about 6 to 12 carbon atoms, and preferably contains about 40% to 80% fluorine by weight, more preferably about 50% to 78% fluorine by weight. The terminal portion of the  $R_f$  radical is a perfluorinated moiety, which will preferably contain at least 7 fluorine atoms. e.g.,  $CF_3CF_2CF_2-$ ,  $(CF_3)_2CF-$ ,  $F_3SCF_2-$ . The preferred  $R_f$  radicals are fully or substantially fluorinated and preferably follow the formula  $C_nF_{2n+1}-$  where n is about 3 to 18.

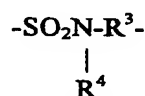
The linking group,  $L^1$ , links the  $R_f$  group to the free radical polymerizable group E.  $L^1$  preferably contains from 1 to about 20 carbon atoms.  $L^1$  can



optionally contain oxygen, nitrogen, or sulfur-containing groups or a combination thereof, and  $L^1$  is preferably free of functional groups that substantially interfere with free-radical oligomerization (e.g., polymerizable olefinic double bonds, thiols, and other such functionality known to those skilled in the art). Examples of suitable

5  $L^1$  groups include straight chain, branched chain or cyclic alkylene, arylene, aralkylene, oxy, oxo, hydroxy, thio, sulfonyl, sulfoxy, amino, imino, sulfonamido, carboxyamido, carbonyloxy, urethanylene, ureylene groups, and combinations thereof such as sulfonamidoalkylene. Preferred linking groups are selected from the group consisting of alkylene groups, poly(oxyalkylene) groups having about 1 to 4

10 oxyalkylene moieties and organic divalent linking groups according to the following formula:



15 wherein:

$R^3$  represents a linear or branched alkylene group having 2 to 4 carbon atoms; and  $R^4$  represents an alkyl group having 1 to 4 carbon atoms.

$R_4$  is a fluorine-free organic group.

E and E' are free radically polymerizable groups that typically contain an

20 ethylenically unsaturated moiety capable of polymerization with itself or each other. Suitable moieties include, for example, those moieties derived from vinyl ethers, vinyl esters, allyl esters, vinyl ketones, styrenes, vinyl amides, acrylamides, maleates, fumarates, acrylates and methacrylates. Of these, the esters of alpha, beta unsaturated acids, such as the acrylates and

25 methacrylates are preferred.

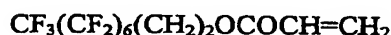
Fluorochemical monomers  $R_4-L^1-E$  as described above and methods for the preparation thereof are known and disclosed, e.g., in U.S. Patent No. 2,803,615. Examples of such compounds include general classes of fluorochemical acrylates, methacrylates, vinyl ethers, and allyl compounds containing fluorinated sulfonamido

30 groups, acrylates or methacrylates derived from fluorochemical telomer alcohols, acrylates or methacrylates derived from fluorochemical carboxylic acids, and perfluoroalkyl acrylates or methacrylates as disclosed in EP-A-526 976.

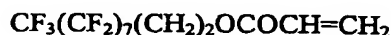
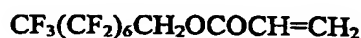
Preferred examples of fluorochemical monomers include :



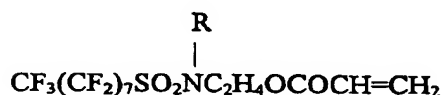
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R=methyl, ethyl or n-butyl.

Suitable hydrocarbon monomers R<sub>n</sub>-E' are also well known and generally commercially available. Examples of such compounds include the general classes of ethylenic compounds capable of free-radical polymerization, such as, for example, allyl esters such as allyl acetate and allyl heptanoate; alkyl vinyl ethers or alkyl allyl ethers such as cetyl vinyl ether, dodecylvinyl ether, 2-chloroethylvinyl ether, ethylvinyl ether; unsaturated acids such as acrylic acid, methacrylic acid, alpha-chloro acrylic acid, crotonic acid, maleic acid, fumaric acid, itaconic acid and their anhydrides and esters such as vinyl, allyl, methyl, butyl, isobutyl, hexyl, heptyl, 2-ethyl-hexyl, cyclohexyl, lauryl, stearyl, isobornyl or alkoxy ethyl acrylates and methacrylates; alpha-beta unsaturated nitriles such as acrylonitrile, methacrylonitrile, 2-chloroacrylonitrile, 2-cyanoethyl acrylate, alkyl cyanoacrylates; alpha, beta-unsaturated carboxylic acid derivatives such as allyl alcohol, allyl

glycolate, acrylamide, methacrylamide, n-diisopropyl acrylamide, diacetoacrylamide, N,N-diethylaminoethylmethacrylate, N-t-butylamino ethyl methacrylate; styrene and its derivatives such as vinyl toluene, alpha-methylstyrene, alpha-cyanomethyl styrene; lower olefinic hydrocarbons which contain halogen such as ethylene, propylene, isobutene, 3-chloro-1-isobutene, isoprene, and allyl or vinyl halides such as vinyl and vinylidene chloride. Preferred co-monomers which can be copolymerized with the above-described fluoroaliphatic radical-containing monomers include those selected from octadecylmethacrylate, laurylmethacrylate, butylacrylate, N-methylol acrylamide, isobutylmethacrylate, ethylhexyl acrylate, ethylhexyl methacrylate, glycidyl methacrylate, vinylchloride and vinylidene chloride.

The hydroxy- or amino-functionalized chain transfer agents useful in the preparation of the fluorochemical oligomer preferably correspond to the following formula:

HS-R-X

wherein:

R is as defined herein and X is an -OH or -NH<sub>2</sub> moiety.

Examples of chain transfer agents include those selected from 2-mercaptoethanol, 3-mercapto-2-butanol, 3-mercapto-2-propanol, 3-mercapto-1-propanol and 2-mercapto-ethylamine. A single compound or a mixture of different chain transfer agents may be used. A preferred chain transfer agent is 2-mercaptoethanol.

In order to prepare the functionalized fluorochemical oligomer, a free-radical initiator is normally present. Such free-radical initiators are known in the art and include azo compounds, such as azobisisobutyronitrile (AIBN) and azobis(2-cyanovaleric acid) and the like, hydroperoxides such as cumene, t-butyl, and t-amyl hydroperoxide, dialkyl peroxides such as di-t-butyl and dicumylperoxide, peroxyesters such as t-butylperbenzoate and di-t-butylperoxy phthalate, diacylperoxides such as benzoyl peroxide and lauroyl peroxide.

In a second step, the fluorochemical oligomer (or mixture of fluorochemical oligomers), the monofunctional compound capable of reacting with an isocyanate

group and difunctional compound capable of reacting with an isocyanate group are reacted with a triisocyanate, to obtain the polyurethane. The reaction may also involve a further isocyanate-reactive compound other than the fluorochemical oligomer and the monofunctional and difunctional compounds. It will be appreciated by one skilled in the art that the preparation of polyurethanes according to the present invention results in a mixture of compounds.

According to a preferred embodiment of the invention, about 6 to 33% of the number of isocyanate groups are reacted with the fluorochemical oligomer, about 33% to 61% of the number of isocyanate groups are reacted with the difunctional compound, about 28 to 35% of the number of isocyanate groups are reacted with the monofunctional compound and 0 to about 10% of the number of isocyanate groups are reacted with a further isocyanate-reactive compound other than the fluorochemical oligomers, the difunctional compound and the monofunctional compound.

Preferably, an oxyalkylene moiety in the poly(oxyalkylene) group of the monofunctional compound has about 2 to 4 carbon atoms. Examples of such moieties include  $-\text{OCH}_2\text{-CH}_2-$ ,  $-\text{OCH}_2\text{-CH}_2\text{-CH}_2-$ ,  $-\text{OCH}(\text{CH}_3)\text{CH}_2-$ , and  $-\text{OCH}(\text{CH}_3)\text{CH}(\text{CH}_3)-$ . The oxyalkylene moieties in the poly(oxyalkylene) group can be the same (e.g., poly(oxypropylene)), or present as a mixture (e.g., a heteric straight or branched chain or a chain of randomly distributed oxyethylene and oxypropylene moieties or a straight or branched chain of blocks of oxyethylene units and blocks of oxypropylene moieties. The backbone of the poly(oxyalkylene) group can be interrupted by or include one or more catenary linkages. Where the catenary linkages have three or more valences, they provide a means for obtaining a branched chain of oxyalkylene moieties. Preferably, the number of oxyalkylene moieties in a poly(oxyalkylene) contained in the monofunctional compound is between about 5 and 120 and more preferably between about 17 and 48.

According to a particularly preferred embodiment, the monofunctional compound corresponds to the following formula:



wherein:

W is selected from the group consisting of O, NH, and S;

R<sup>6</sup> represents an alkylene having about 1 to 4 carbon atoms;

R<sup>7</sup> and R<sup>8</sup> are each independently selected from the group consisting of linear or branched alkylene groups having 2 to 4 carbon atoms;

R<sup>9</sup> represents an alkyl group having about 1 to 4 carbon atoms;

5 x and y are each independently selected integers of 0 to about 60, provided the sum of x and y is at least about 5.

Preferably, R<sup>7</sup> is ethylene and R<sup>8</sup> is a linear or branched propylene and the ratio of x to y is at least 1 and preferably greater than 1. Most preferably, y is 0 and R<sup>7</sup> is ethylene.

10 Typical examples of monofunctional compounds comprising a poly(oxyalkylene) group include alkyl ethers of polyglycols (e.g., methyl or ethyl ether of polyethyleneglycol), hydroxy-terminated methyl or ethyl ether of a random or block copolymer of ethyleneoxide and propyleneoxide or amino-terminated methyl or ethyl ether of polyethyleneoxide.

15 The difunctional compound capable of reacting with an isocyanate group corresponds preferably to the following formula:



wherein:

Y is an organic divalent linking group and

20 X<sup>1</sup> and X<sup>2</sup> are each independently selected from the group consisting of O or NH. Examples of the Y include linear or branched alkylenes, arylenes, aralkylenes or cyclic alkylenes. According to a particularly preferred embodiment of this invention, the difunctional compound is derived from an oligomerisation of one or more fluorine-free monomers as described above in the presence of a chain transfer agent that includes two hydroxy or amino groups or a hydroxy and amino group. An example of such a chain transfer agent is 3-mercapto-1,2-propanediol. More preferably, such oligomer is obtained by an oligomerisation of at least one monomer that contains a functional group capable of cross-linking upon activation, for example, by heat. Typical examples of such functional groups include blocked isocyanates and alkoxysilane groups. Examples of monomers including a functional group capable of cross-linking upon activation include alkoxysilane functionalized

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acrylates or methacrylates or monomers that contain a blocked isocyanate such as the reaction product of 2-hydroxy-ethyl-(meth)acrylate, a diisocyanate and an isocyanate blocking agent. Isocyanate blocking agents for use in this invention are compounds that upon reaction with an isocyanate group yield a group that is

5 unreactive with isocyanate-reactive moieties at room temperature but which reacts at elevated temperatures with isocyanate-reactive moieties. Suitable isocyanate blocking agents will typically react with isocyanate-reactive compounds at a temperature of about 50 to 190°C. Examples of isocyanate blocking agents that can be used include aryl alcohols (e.g., phenols, cresols, nitrophenols, o- and p-

10 chlorophenol, naphthols, 4-hydroxybiphenyl); C<sub>2</sub> to C<sub>8</sub> alkanone oximes (e.g., acetone oxime, butanone oxime); benzophenone oxime; aryl-thiols (e.g., thiophenol); organic carbanion active hydrogen compounds (e.g., diethyl malonate, acetylacetone, ethyl acetoacetate, ethylcyanoacetate) and epsilon-caprolactone. A single compound or a mixture of different masking or blocking agents may be used.

15 Particularly preferred isocyanate blocking or masking agents include C<sub>2</sub> to C<sub>8</sub> alkanone oximes, e.g., 2-butanone oxime. The fluorine-free oligomer preferably has a polymerization degree between about 2 and 40 and more preferably between about 3 and 20.

Further examples of difunctional compounds include alkane diols (e.g., C<sub>2</sub>-

20 C<sub>4</sub> alkane diols like ethylene glycol and 1,4-butanediol), polyester diols, polycaprolactam diols, diamines (e.g., C<sub>2</sub>-C<sub>4</sub> diamines like ethylenediamine), 1,2-diaminopropane, 1,3-diaminopropane, 1,4-diaminobutane, 1,10-diaminodecane, 1,7-diaminoheptane, 1,6-diaminohexane, 1,12-diaminododecane, 1,9-diaminononane, 1,8-diaminooctane, 1,5-diaminopentane, isophoronediamine,

25 piperazine, 1,8-naphthalenediamine, 1,2/1,3/1,4/phenylenediamine, 4-methyl-1,3-phenylenediamine and 4-methyl-1,2-phenylenediamine, and aminoalcohols (e.g., 2-aminobenzylalcohol, 4-amino-1-butanol and ethanolamine).

Triisocyanates for use in accordance with the present invention include aliphatic and aromatic isocyanates. Examples include aliphatic triisocyanates such

30 as 1,3,6-hexamethylenetriisocyanate and aromatic triisocyanates such as polymethylenepolyphenylisocyanate (PAPI), tri-(4-isocyanatophenyl)-methane

(available from Bayer as DESMODUR™ R) and DESMODUR™ L available from Bayer. Also useful are isocyanates containing internal isocyanate-derived moieties such as biuret-containing triisocyanates such as that available from Bayer as DESMODUR™ N-100 and isocyanurate-containing triisocyanates such as that  
5 available from Huls AG, Germany, as IPDI-1890.

The preparation of the fluorochemical compositions comprising polyurethane may optionally include reaction with minor amounts of additional isocyanate-reactive compounds other than those described herein. Such further isocyanate-reactive compounds are typically compounds containing only one  
10 isocyanate-reactive group and include a monofunctional fluorine-free oligomer and an isocyanate blocking agent. Examples of such isocyanate-reactive compounds include alkanols such as methanol, ethanol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, t-butyl alcohol, n-amyl alcohol, t-amyl alcohol, 2-ethylhexanol, glycidol, (iso)stearylalcohol and primary or secondary amines (e.g.,  
15 butyl amine).

The condensation reaction is carried out under conventional conditions well-known to those skilled in the art. Preferably the reaction is run in the presence of a catalyst. Suitable catalysts include tin salts such as dibutyltin dilaurate, stannous octanoate, stannous oleate, tin dibutyldi-(2-ethyl hexanoate), stannous chloride; and  
20 others known to those skilled in the art. The amount of catalyst present will depend on the particular reaction, and thus it is not practical to recite particular preferred concentrations. Generally, however, suitable catalyst concentrations are from about 0.001 percent to about 10 percent, preferably about 0.1 percent to about 5 percent, by weight based on the total weight of the reactants.

25 The condensation reaction is preferably carried out under dry conditions in a polar solvent such as ethyl acetate, acetone, methyl isobutyl ketone, toluene and the like. Suitable reaction temperatures will be easily determined by those skilled in the art based on the particular reagents, solvents, and catalysts being used. While it is not practical to enumerate particular temperatures suitable for all situations,  
30 generally suitable temperatures are between about room temperature and about 120°C.

The fluorochemical composition of this invention can be applied using conventional application methods but is preferably used as an aqueous emulsion. Alternatively it can be used as a treatment composition in solvent. An aqueous emulsion will generally contain water, an amount of fluorochemical composition effective to provide the desired repellent properties to a substrate treated therewith, and a surfactant in an amount effective to stabilize the emulsion. Water is preferably present in an amount of about 70 to 2000 parts by weight based on 100 parts by weight of the fluorochemical composition of the invention. The surfactant is preferably present in an amount of about 1 to 25 parts by weight, preferably about 2 to 10 parts by weight, based on 100 parts by weight of the fluorochemical composition. Conventional cationic, nonionic, anionic, and zwitterionic surfactants are suitable.

The amount of aqueous solvent-based treating composition applied to a substrate should be sufficient to impart high stain release properties to the substrate. Typically, an amount of treating composition sufficient to provide about 0.01% to 5% by weight, preferably about 0.05% to 2% by weight, based on the weight of the substrate, of fluorochemical composition on the treated substrate is adequate. The amount of treatment composition which is sufficient to impart desired stain release properties can be determined empirically and can be increased as necessary or desired.

To the fluorochemical composition of the invention there may also be added other fluorinated products, polymers or auxiliary products such as starch, dextrin, casein, polyvinyl alcohols, cellulose and cellulose derivatives such as cellulose ethers, copolymers of (meth)acrylic acid and an alkyl (meth)acrylate, polyglycols such polyethylene glycols, sizing agents, materials to improve water and/or oil repellency, fire proofing or antistatic properties, buffering agents, fungicidal agents, optical bleaching agents, sequestering agents, mineral salts, surface-active agents, or swelling agents to promote penetration. Preferably, copolymers of an alkyl(meth)acrylate and (meth)acrylic acid are used as auxiliary products in the fluorochemical composition. Typically, the weight ratio of meth(acrylic) acid to alkyl(meth)acrylate in such polymers is between 20:80 and 90:10, and more



preferably between 50:50 and 85:15. It is further preferred that the alkyl group of the (meth)acrylate monomer is a lower alkyl group having about 1 to 6 carbon atoms. Examples of alkyl (meth)acrylates include, methyl, ethyl and n-butyl acrylates and methacrylates. The copolymer of an alkyl (meth)acrylate and  
5 (meth)acrylic acid may further contain units derived from ethylenically unsaturated monomers but preferably the copolymer only consists of units or moieties derived from alkyl (meth)acrylates and (meth)acrylic acid. The copolymer may also be partially or fully neutralized with a base such as sodium hydroxide or ammonium hydroxide.

10 Particularly suitable auxiliary products for use in the fluorochemical composition include polyvinyl alcohols and non-ionic cellulose ethers. Examples of non-ionic cellulose ether derivatives include methyl cellulose, hydroxypropyl cellulose and methylhydroxypropyl cellulose. Preferably, the etherified cellulose is highly hydrophilic. Accordingly, cellulose ethers that contain large hydrophobic  
15 substituents such as the hydrophobically modified cellulose ether (available under the trade name NEXTON™ from Aqualon) are not preferred for use in the fluorochemical composition of this invention.

The substrates treated by the fluorochemical composition of this invention are not especially limited and include plastic, metal, glass, fibrous materials such as  
20 textile fabrics, wood, non-wovens and paper. The fluorochemical composition is particularly useful for imparting stain release properties to a substrate that comprises natural fibers, in particular a substrate that consists of cellulose fibers or a substrate consisting of cellulose and polyester fibers. Substrates treated with a fluorochemical composition of this invention have particular good stain release  
25 properties for dirty motor oil stains and tea stains.

In order to affect treatment of a textile substrate, the substrate can be immersed in a diluted emulsion. The saturated substrate can then be run through a  
padder/roller to remove excess emulsion, dried and cured in an oven at a  
temperature and for a time sufficient to provide a cured treated substrate. This  
30 curing process is typically carried out at temperatures between about 50°C and 190°C depending on the particular system or application method used. In general, a

temperature of about 120°C to 170°C, in particular of about 150°C to 170°C for a period of about 20 seconds to 10 minutes, preferably 3 to 5 minutes, is suitable.

The invention is further illustrated by reference to the following examples without however the intention to limit the invention thereto.

5

## EXAMPLES

### Formulation and Treatment Procedure

Treatment baths were formulated containing a defined amount of the fluorochemical treatment agent. Treatments were applied to the test substrates by padding to provide a concentration of 0.3% or 0.6% solids (based on fabric weight and indicated as SOF (solids on fabric)) and drying the samples at 150°C during 3 minutes. The test substrates used in the Examples were commercially available and are listed below:

\* PES/CO : polyester/cotton 67/33 blends, available from Arlitex, Avelgem, Belgium.

\* 100% cotton : available from UCO company, Destelbergen, Belgium

After drying, the substrates were tested for their stain release and repellency properties.

Respective data of stain release, water and oil repellency shown in the Examples and Comparative Examples were based on the following methods of measurement and evaluation criteria :

### Stain Release Test

The stain release test was performed using two types of stains :

- Dirty Motor Oil (DMO) obtained from General Motors Garage Houttequiet, Beveren; Belgium
- Tea : obtained by immersing a Lipton™ yellow teabag in 165 ml water at 65°C for a period of 3 minutes

Staining Procedure 1 : Drop Method

10 cm x 10 cm test samples were stained with 3 drops DMO or tea for PES/CO or with 4 drops DMO or tea for cotton. The samples were equilibrated at room temperature during 24 hours after which the degree of staining was evaluated by measuring the difference in reflection of a stained versus unstained sample, using a Minolta color meter (Lamp D65). An average of 3 measurements were done for each stain, resulting in a  $\Delta L_{IN}$  value.

Staining Procedure 2 : Brush Method

For this procedure, 0.35 ml DMO or 0.5 ml tea for PES/CO or 0.5 ml DMO or 0.6 ml tea for cotton were placed on 10 cm x 10 cm test samples. The stain was brushed into the fabric by brushing 3 times around in a plastic holder of 5 cm diameter placed around the staining liquid. The reflection measurement was done as described above.

Laundering procedure

The test samples were pinned on a PES/CO ballast (total 3 kg) or a cotton ballast (total 4 kg), and laundered in a Miele washing machine type W 832. A commercial detergent (20 g/kg Clax 100 for PES/CO or Clax crystal for cotton, available from Diversy Lever) was added and the substrates were washed at 70°C, using the main washing program, followed by four rinse cycles and centrifuging. The samples were dried in a tumble dryer and ironed at 150°C for 15 seconds. Unstained samples were treated the same way. The samples were measured with the Minolta meter and compared to unstained samples, resulting in a  $\Delta L_{LD70^{\circ}C}$  value.

The less negative value for  $\Delta L_{LD70^{\circ}C}$  obtained compared to  $\Delta L_{IN}$ , the better the stain release properties were.  $\% \Delta \Delta L$ , calculated according to formula

$$\% \Delta \Delta L = (\Delta L_{IN} - \Delta L_{LD70^{\circ}C} / \Delta L_{IN}) \times 100$$

gave an indication of the percentage of stain removed during the laundering process. The higher the value, the better the stain removal.

**Water Repellency Test (WR)**

- The water repellency (WR) of a substrate was measured using a series of water-isopropyl alcohol test liquids and was expressed in terms of the "WR" rating of the treated substrate. The WR rating corresponded to the most penetrating test liquid which did not penetrate or wet the substrate surface after 15 seconds exposure. Substrates which were penetrated by or were resistant only to 100% water (0% isopropyl alcohol) test liquid, the least penetrating test liquid, were given a rating of 0. Substrates resistant to test liquids which were 100% isopropyl alcohol (0% water), the most penetrating test liquid, were given a rating of 10. Other intermediate ratings were calculated by dividing the percent isopropyl alcohol in the test liquid by 10, e.g., a treated substrate resistant to a 70%/30% isopropyl alcohol/water blend, but not to an 80%/20% blend, would be given a rating of 7.

**Oil Repellency (OR)**

- The oil repellency of a substrate was measured by the American Association of Textile Chemists and Colorists (AATCC) Standard Test Method No. 118-1983, which test was based on the resistance of a treated substrate to penetration by oils of varying surface tensions. Treated substrates resistant only to Nujol® mineral oil (the least penetrating of the test oils) were given a rating of 1, whereas treated substrates resistant to heptane (the most penetrating of the test liquids) were given a rating of 8. Other intermediate values were determined by use of other pure oils or mixtures of oils, as shown in the following table.

**Standard Test Liquids**

<b>AATCC Oil Repellency Rating Number</b>	<b>Compositions</b>
1	Nujol®
2	Nujol® /n-Hexadecane 65/35
3	n-Hexadecane
4	n-Tetradecane
5	n-Dodecane

AATCC Oil Repellency Rating Number	Compositions
6	n-Decane
7	n-Octane
8	n-Heptane

### Abbreviations

The following abbreviations and trade names were used in the Examples and Comparative Examples :

- 5
- EtOAc : ethylacetate  
RSH : 2-mercapto ethanol  
MPD : 3-mercapto-1,2-propanediol  
AIBN : azo(bis)isobutyronitrile
- 10 MEFOSEA : N-methyl perfluorooctyl sulfonamido ethyl acrylate  
MPEG <sup>750-2000</sup> : polyethylene glycol methyl ether, the superscript number is indicative of Mw, available from Inspec, Belgium  
HOEMA : 2-hydroxyethyl methacrylate  
IPDI : isophorone diisocyanate
- 15 BA : n-butylacrylate  
GMA : glycidyl methacrylate (2,3-epoxypropyl methacrylate)  
BO : 2-butanone oxime  
DBTDL : dibutyltin dilaurate  
MEHQ : methylhydroquinone
- 20 DESN : aliphatic polyisocyanate, available from Bayer (Germany) as DESMODUR™ N  
Arquad T-50 : tallow trimethyl ammonium chloride, available from Akzo, Littleborough, UK
- 25 All parts, ratios, percentages etc. in the following examples are by weight unless otherwise noted.

A. Synthesis of Hydroxyterminated Oligomers (HTO)

1. Synthesis of Urethane Acrylate HOEMA/IPDI/BO (molar ratio 1/1/1)

The urethane acrylate HOEMA/IPDI/BO (molar ratio 1/1/1), used in the preparation of hydroxy terminated oligomers was prepared as follows :

- 5 A round bottom flask equipped with a mechanical stirrer, a temperature control, addition funnel, and nitrogen inlet and outlet, was charged with 111 g (0.5 moles) IPDI, 65 g (0.5 moles) HOEMA, 200 g EtOAc, 0.1 g phenotiazin, 0.1 g MEHQ and 0.2 g dibutyl tin dilaurate. The reaction mixture was slowly heated to about 50°C. A solution of 44 g (0.5 moles) 2-butanone oxime, dissolved in 20 g EtOAc was added over a period of 1 hour. Then the reaction mixture was stirred at 10 72°C for 6 hours. IR analysis indicated that all isocyanate groups had reacted.

2. Synthesis of hydroxy terminated oligomers (HTO)

- Hydroxy terminated oligomers (HTO) as given in Table 1 were made using a procedure similar to the synthesis of MEFOSEA/RSH 4/1 (indicated as HTO-1 in 15 Table 1):

A round bottom flask equipped with two reflux condensers, a stirrer, a temperature control, a nitrogen inlet and a vacuo outlet was charged with 2.4 moles (1433 g) MEFOSEA and 987 g EtOAc. The mixture was heated at 40°C until all 20 fluorochemical monomers were dissolved. 0.6 moles (46.8 g) 2-mercaptoethanol and 0.15% AIBN were added. The reaction mixture was gradually heated to 80°C. The reaction was run under nitrogen atmosphere at 80°C for 16 hours, after which more than 95% conversion was obtained.

**Table 1 : Composition of hydroxy terminated oligomers (HTO)**

Oligomer	Composition	Molar Ratio
HTO-1	MEFOSEA/RSH	4/1
HTO-2	MEFOSEA/RSH	8/1
HTO-3	BA/GMA/MPD	4/1/1
HTO-4	(HOEMA/IPDI/BO)/BA/MPD	1/3/1

**B. Synthesis of fluorochemical compounds (FC)**

Several of the fluorochemical compounds listed in Table 2 were prepared using a procedure similar to the following synthesis of DESN/HTO-1/HTO-4/MPEG<sup>750</sup> (2/2/1/2) (FC-1 in Table 2):

- 5 A round bottom flask equipped with a condensor, thermometer, stirrer and nitrogen inlet was charged with 22.32 g (0.025 moles) Desmodur N100, 11.65 g (0.0125 moles) HTO-4, 63.05 g (0.025 moles) HTO-1 and 18.75 g (0.025 moles) MPEG<sup>750</sup>, followed by 257 g ethyl acetate. The reaction mixture was heated to 50°C after which catalyst was added (DBTDL). The temperature of the mixture  
10 was raised to 75°C and the reaction was run until completion.

**C. Emulsification**

- The fluorochemical compound obtained under step B (20 g solids) was added to deionised water containing 1.2 g Arquad T-50 (50% solids) emulsifier.  
15 The mixture was homogenized using an ultrasonic probe (Branson 250 sonifier) after which the organic solvent was removed under vacuum. An emulsion containing 15% fluorochemical compound was obtained.

**Table 2: Composition of Fluorochemical Urethanes (FC)**

FC	Composition of Fluorochemical Compound	Molar Ratio
FC-1	DESN/HTO-1/HTO-4/MPEG <sup>750</sup>	2/2/1/2
FC-2	DESN/HTO-1/HTO-4/MPEG <sup>750</sup>	3/2/2/3
FC-3	DESN/HTO-2/HTO-4/MPEG <sup>2000</sup>	2/2/1/2
FC-4	DESN/HTO-1/HTO-3/MPEG <sup>750</sup>	2/2/1/2

20

**Examples 1 and 2 and Comparative Example C-1**

- In Examples 1 and 2, fluorochemical compounds according to the invention were prepared and emulsified following the general procedure described above. Polyester/cotton (PES/CO) blends were treated with the fluorochemical compounds  
25 to provide 0.6 % SOF. After treatment, the fabrics were dried at 150°C for 3 minutes. The treated PES/CO substrates were stained with dirty motor oil using the

drop method. Comparative Example C-1 was made with untreated PES/CO fabric. The results for stain release and oil and water repellency are given in Table 3.

**Table 3 : Stain Release (DMO-Drop) and Repellency Properties of Treated PES/CO**

Ex No	Fluorochemical Compound	% SOF	Initial Performance		Stain Release Color Measurement		
			OR	WR	$\Delta L_{IN}$	$\Delta L_{LD70^{\circ}C}$	% $\Delta\Delta L$
1	FC-1	0.6	5	8	-6.25	-0.84	87
2	FC-4	0.6	5	7	-6.35	-1.83	71
C-1	--	--	0	0	-15.45	-9.56	38

The data shows that the fluorochemical compounds according to the invention provide very good DMO stain release. Besides good stain release properties, also good to very good oil and water repellency properties were obtained, presenting a further advantage.

**Examples 3 and 4 and Comparative Example C-2**

In Examples 3 and 4, the same type of experiment was repeated but this time the DMO was applied to the fabric by the brush method. Comparative Example C-2 was made with untreated PES/CO fabric. The results of stain release and oil and water repellency are given in Table 4.

**Table 4 : Stain Release (DMO-Brush Method) and Repellent Properties of Treated PES/CO**

Ex No	Fluorochemical Compound	% SOF	Initial Performance		Stain Release Color Measurement		
			OR	WR	$\Delta L_{IN}$	$\Delta L_{LD70^{\circ}C}$	% $\Delta\Delta L$
3	FC-2	0.6	5	9	-18.06	-9.68	46
4	FC-3	0.3	3	4	-18.26	-9.59	47
C-2	--	--	0	0	-15.32	-8.67	43



Examples 5 and 6 and Comparative Example C-3

In Examples 5 and 6, the same type of experiment as above was repeated with 100% cotton substrates, treated with the fluorochemical compositions according to the general procedure as described above. DMO stain was applied to the cotton using the brush method. Comparative Example C-3 was made with untreated cotton fabric. The results of stain release and oil and water repellency are given in Table 5.

**Table 5 : Stain Release (DMO-Brush Method) and Repellent Properties of Treated Cotton**

Ex No	Fluorochemical Compound	% SOF	Initial Performance		Stain Release Color Measurement		
			OR	WR	$\Delta L_{IN}$	$\Delta L_{LD70^{\circ}C}$	% $\Delta\Delta L$
5	FC-2	0.3	2	3	-18.45	-7.93	57
6	FC-3	0.3	2	4	-19.7	-7.92	60
C-3	--	--	0	0	-15.70	-8.76	44

The data shows that a good percentage of stain removal (% $\Delta\Delta L$ ) was observed for oily stains such as DMO on cotton substrates.

Examples 7 and 8 and Comparative Example C-4

In Examples 7 and 8, PES/CO blends treated with the fluorochemical compounds according to the invention were stained with tea using the drop method. Comparative Example C-4 was made with untreated fabric. The results of stain release and oil and water repellency are given in Table 6.

**Table 6 : Stain Release (Tea-Drop Method) and Repellent Properties of Treated PES/CO**

Ex No	Fluorochemical Compound	% SOF	Initial Performance		Stain Release Color Measurement		
			OR	WR	$\Delta L_{IN}$	$\Delta L_{LD70^{\circ}C}$	% $\Delta\Delta L$
7	FC-1	0.6	5	8	-3.92	-0.26	93
8	FC-4	0.6	5	7	-6.96	-0.79	89
C-4	--	--	0	0	-2.32	-0.91	61

A high percentage of tea stain removal was observed on the treated samples.

**Examples 9 and 10 and Comparative Example C-5**

- 5 In Examples 9 and 10, PES/CO substrates treated with the fluorochemical compounds according to the invention were tested with tea stains, but now using the brush method. Comparative Example C-5 was made with untreated material. The results of stain release and oil and water repellency are given in Table 7.

10 **Table 7 : Stain Release (Tea-Brush Method) and Repellent Properties of Treated PES/CO**

Ex No	Fluorochemical Compound	% SOF	Initial Performance		Stain Release Color Measurement		
			OR	WR	$\Delta L_{TN}$	$\Delta L_{LD70^{\circ}C}$	% $\Delta\Delta L$
9	FC-2	0.6	5	9	-1.32	-0.77	42
10	FC-3	0.3	4	6	-1.42	-0.66	54
C-5	—	—	0	0	-2.62	-1.22	53

- 15 Although the percentage stain removal for the tea stain was not better or even inferior than the untreated samples, the treated samples showed a much less negative value for  $\Delta L_{LD70^{\circ}C}$  than the untreated sample, indicating a less visible stain after laundering in case of the samples treated with a fluorochemical composition of the invention.

20 **Examples 11 and 12 and Comparative Example C-6**

In Examples 11 and 12, cotton substrates treated with the fluorochemical compositions of the present invention were stained with tea using the brush method. Comparative Example C-6 was made with untreated material. The results of stain release and oil and water repellency are given in Table 8.

25

**Table 8 : Stain Release (Tea-Brush Method) and Repellent Properties of Treated Cotton**

Ex No	Fluorochemical Compound	% SOF	Initial Performance		Stain Release Color Measurement		
			OR	WR	$\Delta L_{TN}$	$\Delta L_{LD70^{\circ}C}$	% $\Delta\Delta L$
11	FC-2	0.3	2	3	-2.04	-0.46	77
12	FC-3	0.3	2	3	-2.24	-0.32	86
C-6	—	—	0	0	-3.21	-1.36	58

- 5           The results indicate that cotton fabric treated with the fluorochemical compounds of the invention showed high tea stain removal.

## CLAIMS

1. A method for preparing a fluorochemical composition comprising a polyurethane by reacting:

- 5 (A) fluorochemical oligomer of formula (I)



wherein:

$M_m^f M_n$  represents fluorochemical oligomer comprising m units derived from fluorinated monomer and n units derived from fluorine-free monomer and wherein the fluorinated monomers and fluorine-free monomers may be the same or different;

m represents a value of 2 to 40;

n represents a value of 0 to 20;

$T^1$  is -OH or -NH<sub>2</sub>;

- 15  $Q^1$  and  $T^1$  together represent an organic residue obtained by removing a hydrogen atom from a chain transfer agent that is functionalized with  $T^1$ ;

(B) difunctional compound capable of reacting with an isocyanate; and

(C) monofunctional compound capable of reacting with an isocyanate and comprising a poly(oxyalkylene) group; with

- 20 (D) triisocyanate.

2. A method according to claim 1, wherein said fluorinated monomer corresponds to the following formula:



- 25 wherein:

$R_f$  is selected from the group consisting of perfluorinated or partially fluorinated aliphatic groups;

$L^1$  represents an organic divalent linking group and;

E represents a free radical polymerizable group.

30

3. A method according to claim 2, wherein E is an acrylate or a methacrylate group, and  $L^1$  is selected from the group consisting of alkylenes,

poly(oxyalkylenes) having 1 to 4 oxyalkylene moieties, and organic divalent linking group according to the following formula:



5

wherein:

R<sup>3</sup> is selected from the group consisting of linear or branched alkylenes having 2 to 4 carbon atoms; and

R<sup>4</sup> represents an alkyl group having 1 to 4 carbon atoms.

10

4. A method according to any of the previous claims, wherein Q<sup>1</sup> corresponds to the formula:

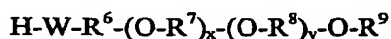


wherein:

15 R represents an organic divalent linking group selected from the group consisting of linear or branched alkylenes, cyclic alkylenes and arylenes.

5. A method according to any of the previous claims, wherein said monofunctional compound comprising a poly(oxyalkylene) group corresponds to the following formula:

20



wherein:

W is selected from the group consisting of O, NH, and S;

R<sup>6</sup> represents an alkylene group having 1 to 4 carbon atoms;

25 R<sup>7</sup> and R<sup>8</sup> are each independently selected from the group consisting of linear or branched alkylenes having 2 to 4 carbon atoms;

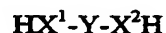
R<sup>9</sup> represents an alkyl group having 1 to 4 carbon atoms;

x is an integer of 0 to 60;

y is an integer of 0 to 60; and

30 the sum of x and y is at least 5.

6. A method according to any of claims 1 to 5, wherein said difunctional compound used to prepare said fluorochemical compositions corresponds to the following formula:



5 wherein:

Y represents an organic divalent linking group selected from the group consisting of linear or branched alkylenes, cyclic alkylenes, arylenes and aralkylenes;

X<sup>1</sup> is O or NH; and

X<sup>2</sup> is O or NH.

10

7. A method according to claim 6, wherein said difunctional compound is derived from an oligomerization of one or more fluorine-free monomers in the presence of a chain transfer agent that includes two functional groups which are each independently selected from the group consisting of hydroxy or amino groups.

15

8. A method according to claim 7, wherein at least one of said fluorine-free monomers contains a functional group capable of cross-linking upon activation by heat.

20

9. A method according to any of the previous claims, wherein 6 to 33% of the number of isocyanate groups are reacted with said fluorochemical oligomer, 33% to 61% of the number of isocyanate groups are reacted with said difunctional compound, 28 to 35% of the number of said isocyanate groups are reacted with said monofunctional compound, and 0 to 10% of the number of isocyanate groups are reacted with an isocyanate-reactive compound other than said fluorochemical oligomers, said difunctional compound and said monofunctional compound.

25

10. A fluorochemical composition obtainable by the method of any of claims 1 to 9.

30

11. A fluorochemical composition according to claim 10, further comprising a polymer selected from the group consisting of polyvinyl alcohols, copolymers of (meth)acrylic acid and alkyl esters of (meth)acrylic acid, polyethylene glycols and non-ionic cellulose ethers.
- 5
12. A method of treatment of a substrate comprising the step of contacting said substrate with a fluorochemical composition according to claim 10 or 11.
- 10
13. A method according to a claim 12, wherein said substrate is a fibrous substrate.
14. A method according to claim 13, wherein said substrate comprises natural fibers.
- 15
15. A method according to claim 13, wherein said substrate is fibrous and the fibers are selected from the group consisting of cellulose fibers, polyester fibers, and blends thereof.
- 20
16. Use of a fluorochemical composition of claim 11 or 12 to impart stain release properties to a substrate.
17. A substrate comprising on at least part of at least one surface a fluorochemical composition according to claim 11 or 12.

# INTERNATIONAL SEARCH REPORT

National Application No

PCT/US8/09797

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC 6 C08G18/28 C08G18/62 D06M15/576 D06M13/428

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
 IPC 6 C08G D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96 12059 A (DU PONT) 25 April 1996 see claims 1,2,4,7,12 see page 5, line 4 - page 7, line 36 & US 5 509 939 A cited in the application ---	1
A	WO 92 17635 A (MINNESOTA MINING & MFG) 15 October 1992 see claims 1-7,27,29,42 see page 12, line 43 - page 19, line 15 & US 5 276 175 A cited in the application -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

**\* Special categories of cited documents :**

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

13 July 1998

Date of mailing of the international search report

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9612059	A	25-04-1996	US 5509939 A	23-04-1996
			AU 3830495 A	06-05-1996
WO 9217635	A	15-10-1992	US 5276175 A	04-01-1994
			BR 9205842 A	02-08-1994
			CA 2105301 A	03-10-1992
			DE 69204831 D	19-10-1995
			DE 69204831 T	28-03-1996
			EP 0578651 A	19-01-1994
			JP 6506239 T	14-07-1994
			US 5453540 A	26-09-1995

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